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RED SLIME FROM ALUMINA PRODUCTION AS MATERIAL FOR TINTED GLAZES

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The possibility of introducing red bauxite slime into the composition of raw glaze is analyzed. Dull pigment-free glaze coatings of a black color have been developed, and the crystalline phases formed in firing of the glaze layer have been identified.

The industrial regions of the CIS involved in the production of alumina generate large quantities of waste in the form of red bauxite slime. This waste, which occupies large areas of fertile land and has a damaging effect on the environment, can, in turn, be an additional source of materials for several sectors of industry. Bauxite slime in its chemicomineralogical composition resembles certain natural materials and can be effectively used to replace traditional materials used in ceramic production.

There are data [1] on the production of glaze coatings, in particular of pink and cream colors and good luster with the content of red bauxite slime equal to 14 – 22%.[2]

The purpose of our study is to study the possibility of using red bauxite slime in the production of dull black glaze coatings for fine ceramics, which currently enjoy high consumer demand. The development of such vitreous coatings will make it possible to expand the range of available materials and obtain a good decorative effect on ceramics with a low production cost.

The development of the specified coatings was carried out on the basis of raw transparent glazes containing pegmatite, quartz sand, kaolin, chalk, talcum, zinc white, and barium carbonate using the waste in the form of red bauxite slime generated in the production of alumina at the Dnepropetrovsk Aluminum Works.

The red slime powder has the following chemical composition (%): 44.50 ($Fe_2O_3 + FeO$), 16.60 Al_2O_3, 9.07 SiO_2, 8.05 CaO, 5.80 Na_2O, and 5.71 TiO_2. Its mineralogical composition is represented by sodalite-like sodium hydroaluminosilicate, hydrogarnets $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 6H_2O$ and $3CaO \cdot (Al, Fe)_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, hematite, calcite rutile, and a titanium-bearing complex of the type of perovskite $CaO \cdot TiO_2$ [2 – 4].

The specified chemical and mineralogical composition of slime, as well its is high dispersion, make it suitable as a component for raw glaze.

To develop a dull black vitreous coating, the main low-melting component (pegmatite) in the initial glaze composition was consecutively replaced by red slime at 10 % intervals until the pegmatite was totally excluded. It was found that to obtain a dull black coating, one has to introduce 40% or more of red slime into the experimental raw glaze composition instead of pegmatite. Such coatings fired at a temperature of 1200°C have good fusion and spreading and the following main parameters: coefficient of diffuse reflection (CDR) 4.72 – 5.04%, luster 18 – 25%, color tone 400 – 460 nm, color purity 2%, and TCLE calculated according to Winkelman and Shott $(10.19 - 11.08) \times 10^{-6} K^{-1}$. At the same time, it should be noted that when more than 40% pegmatite is replaced by bauxite slime, a mesh of microcrakcs is formed in the glaze layer, which becomes more intense as the content of the waste in the raw glaze suspension increases.

In order to decrease the TCLE of experimental glass-ceramic coatings and verify the possibility of excluding costly flux components from the glaze composition, ZnO and $BaCO_3$ were replaced by quartz sand and MgO was introduced via technical magnesite instead of talc.

The prepared glaze slips had good rheological properties and could be easily deposited (by casting) on predried porcelain samples. The coatings were fired in an electric laboratory furnace at a maximum temperature of 1200°C with an exposure of 1 h.

The qualitative and optical-color characteristics of the glaze coatings obtained are listed in Table 1.

A low CDR (4.82 – 5.15%) and the optical characteristic values point to the black color of the dull coatings. At the same time, it should be noted that coating 1 with the molar ratio $SiO_2 : Al_2O_3$ equal to 6.21 has insufficient homogeneity, which is manifested by occasional small sites with weak

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[2] Here and elsewhere mass content indicated.

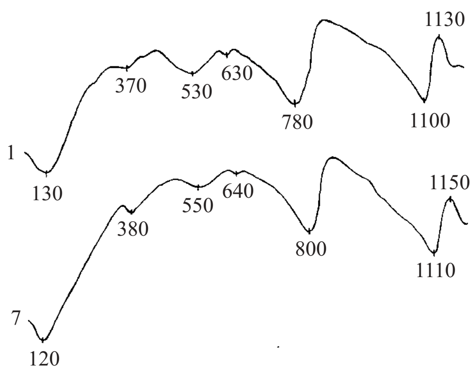

Fig. 1. Thermograms of glaze mixtures 1 and 7.

luster. This is presumably due to incomplete crystallization under the preset firing conditions caused by a high viscosity of the glaze melt due to its high content of silica [5, 6]. Crackle is observed on coatings 2 and 3 caused by an increased TCLE in the glazes.

Considering the above experimental and literature [7, 8] data, 0.5 – 3.0 weight fractions of finely dispersed technical alumina were additional introduced in the experimental raw glazes in milling (to raise the crystallization capacity of the vitreous coatings) (Table 2).

The values of optical and color characteristics, as well as evaluation of the quality of fired coatings, established that the optimum quantity of technical alumina additive to produce a dull black glaze is 1 – 2 weight fractions. The devitrified coating in this case has a saturated black color, which is corroborated by sufficiently low values of the CDR (5.3 – 5.6%), weak luster (19 – 21%), color tone 470 – 490 nm, color purity 2 – 3%, as well as good continuity and absence of crackle. The best quality in the coating was obtained with glaze 7.

Differential-thermal analysis of glaze mixtures 1 and 7 indicated (Fig. 1) the presence of endothermic effects in the temperature intervals of 120 – 130, 530 – 550, and 780 – 800°C caused by the removal of adsorbed and chemically bound moisture, respectively, as well as decarbonizing of $CaCO_3$. The dehydration of hematite FeOOH and its transformation into hematite α-Fe_2O_3 corresponds to an endothermic effect at temperatures 370 – 380°C, and the reversible polymorphic transformation of α-Fe_2O_3 into γ-Fe_2O_3 corresponds to the effect at 630 – 640°C. The endothermic effect in the temperature interval of 1100 – 1110°C is due to the formation of feldspar melts and the peak at 1130 – 1150°C to the crystallization of anorthite, whose presence in the vitreous coating is corroborated by the data of x-ray phase analysis (Fig. 2). The shift of the exothermic effect and the majority of the endothermic effect to a higher-temperature range can be attributed to the additional introduction of γ-Al_2O_3 in the glaze composition, which makes it higher-melting.

X-ray phase analysis established the presence of hematite α-Fe_2O_3 and a stable triclinic form of anorthite $Ca[Al_2Si_2O_8]$ in the dull glaze compositions, taking 35 and 65%, respectively, of the total crystalline phase. At the same time, the diffraction maxima of the specified compounds are more intense in glass 7 containing 2 additional weight fractions of technical alumina, which points to a more complete crystallization in the melt under the particular firing condi-

TABLE 1

Experimental coating	Quantity of slime introduced in glaze, %	$SiO_2 : Al_2O_3$ ratio	TCLE, $10^{-6}\,K^{-1}$	CDR, %	Luster, %	Color tone, nm	Color purity, %	Visual estimate of color and quality of coating
1	40	6.21	9.96	5.15	24	489	3	Surface with a black color, smooth, dull, with occasional lustrous sites
2	45	5.76	10.32	5.10	19	487	3	Surface of a black color, smooth, dull, with crackle
3	50	5.08	10.82	4.82	17	573	1	The same

TABLE 2

Experimental coating	Quantity of introduced γ-Al_2O_3, wt. parts	$SiO_2 : Al_2O_3$ ratio	TCLE, $10^{-6}\,K^{-1}$	CDR, %	Luster, %	Color tone, nm	Color purity, %	Visual estimate of color and quality of coating
4	0.5	5.99	10.00	5.23	25	488	3	Surface with a black color, smooth, dull, with occasional lustrous sites
5	1.0	5.78	10.03	5.43	21	490	3	Surface of a black color, smooth, dull
6	1.5	5.55	10.07	5.60	20	490	2	The same
7	2.0	5.36	10.10	5.30	19	470	2	″
8	3.0	5.02	10.16	5.12	17	573	1	Surface of a black color, dull, with crystallization

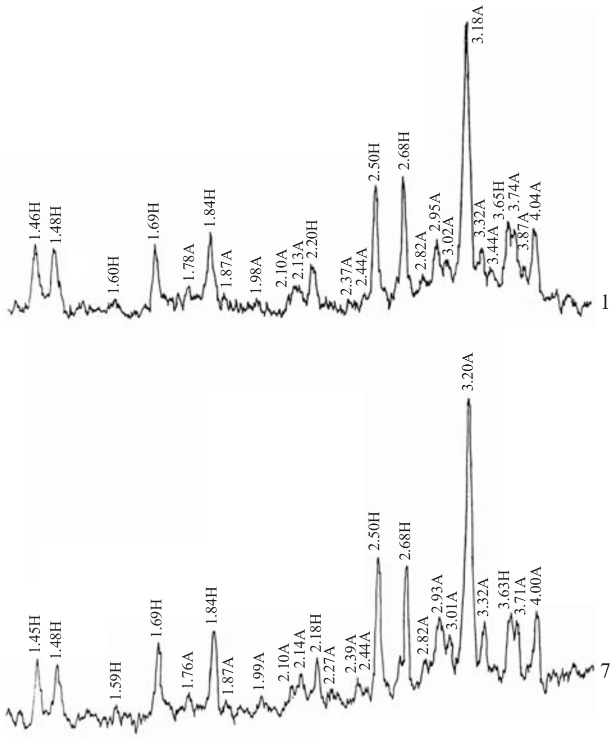

Fig. 2. X-ray patterns of dull black coatings 1 and 7 fired at 1200°C: H) hematite, A) anorthite.

tions. This is supported by the good quality of glaze and the low luster parameter (Table 2).

The presence of hematite, whose crystals can vary in color from light gray to yellow-black and form continuous solid solutions with aluminum oxides [9] in the fired glaze layer, is presumably due to an incomplete dissolution of hematite in the glaze melt and determines the formation of black glass-ceramic coatings.

Thus, the use of the waste from alumina production (red bauxite slime) makes it possible to produce pigment-free glass-ceramic coatings of a black color. The crystalline phases formed in the glaze coating under firing are hematite and anorthite. The formation of a dull finely crystalline coating texture is facilitated by finely disperse technical alumina added into the mixture.

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